# **PROPOSED**

# BEST DEMONSTRATED AVAILABLE TECHNOLOGY (BDAT) BACKGROUND DOCUMENT FOR DYES AND PIGMENTS PRODUCTION WASTES

U.S. Environmental Protection Agency Office of Solid Waste Ariel Rios Building (5302W) 1200 Pennsylvania Avenue N.W. Washington, D.C. 20460

September 17, 2003

# **DISCLAIMER STATEMENT**

The mention of commercial products or trade processes; their source or vendor; or their use in connection with material reported herein should not be construed as either an actual or implied endorsement of such products/services by the U.S. Environmental Protection Agency.

#### **EXECUTIVE SUMMARY**

This background document provides EPA's rationale and technical support for developing Land Disposal Restrictions (LDR) treatment standards for nonwastewaters generated by dye/pigment manufacturing that, at the point of generation, meet the listing description proposed as hazardous waste number K181.

EPA is proposing to prohibit the land disposal of both nonwastewater and derived wastewater forms of Hazardous Wastes K181, unless these wastes are in compliance with the LDR treatment standards being proposed today. Specifically, EPA is proposing numerical standards for the majority of the constituents of concern in K181 wastes. Alternatively, EPA is also proposing the option of a technology-specific treatment standard of combustion (CMBST) for nonwastewater forms. For wastewater forms of these wastes, EPA is proposing the option of a technology-specific treatment standard consisting of any one of the following treatment trains: (1) the treatment train consisting of wet air oxidation (WETOX) followed by carbon adsorption (CARBN); (2) the treatment train consisting of chemical oxidation (CHOXD) followed by carbon adsorption (CARBN); or (3) treatment by combustion (CMBST). Each of these technologies are currently defined in 40 CFR §268.42.

#### Characterization of Wastes

EPA found that, as generated, the K181 wastes would likely meet the definition of "nonwastewater" under 40 CFR 268.2(f). To meet the definition of nonwastewater, wastes must have one percent or more total suspended solids (TSS) or one percent total organic carbon (TOC). However, through treatment facilities may generate K181 with TSS or TOC levels less than these levels, and be classified as wastewaters for application of the land disposal restriction treatment requirements. Thus, there may be both wastewater and nonwastewater forms of K181.

In developing the BDAT treatment standards proposed today, EPA considered the contaminants likely to be present in the wastes. EPA limited its consideration to the contaminants proposed as the basis for listing these wastes. These contaminants were proposed

as the basis for listing following the review of data obtained from publicly available information about the industry, and evaluation of the risks posed by the specific constituents.

# **Development of Treatment Standards**

EPA identified technologies that are applicable and demonstrated for treating the constituents expected to be present in K181 wastes. For the organic constituents identified as the basis for listing these wastes, EPA identified treatment performance data for these constituents (as available), and found chemical/physical properties and chemical structures for all constituents identified as the basis for listing. EPA found that the most difficult to treat of the constituents could be adequately treated using incineration, to levels below analytical detection in the treatment residual. Based on this evaluation, EPA expects treatment by combustion to best treat each of the contaminants proposed as the basis for listing, as well as similar organic contaminants that may be present.

For derived wastewaters, EPA also identified technologies that are either (1) applicable and demonstrated for treating the constituents expected to be present in K181 wastes, or (2) applicable and demonstrated for treating the more general class of "dye and pigment production wastewaters," which may contain some of these contaminants identified as the basis for listing. As with its evaluation of nonwastewaters above, EPA identified treatment performance data for these constituents (as available), and found chemical/physical properties and chemical structures for all constituents identified as the basis for listing. EPA also used the literature to identify technologies effective in reducing concentrations of indicator parameters (e.g., chemical oxygen demand) in dye and pigment production wastewaters. Based on this evaluation, EPA identified that several treatment trains that can be used to adequately treat each of the contaminants proposed as the basis for listing, as well as similar contaminants that may be present. The treatment trains are: (1) the treatment train consisting of wet air oxidation (WETOX) followed by carbon adsorption (CARBN); (2) the treatment train consisting of chemical oxidation (CHOXD) followed by carbon adsorption (CARBN); or (3) treatment by combustion (CMBST).

Even using the data sources described above (i.e., available treatment data, physical/chemical/structural properties), there are data gaps which made assessing technology performance for some constituents difficult. While we expect the above technologies to substantially diminish the toxicity of all compounds, as required by statute, the same degree of supporting data was not available for all constituents.

EPA also assessed the potential of developing numerical standards for those constituents with current technology based treatment standards and those other constituents of concern in K181 that lack current treatment requirements. Numerical treatment standards have been promulgated for only two of the organic constituents of concern. One constituent of concern has existing technology based treatment requirements. Commenters to the July 23, 1999, listing proposal (64 FR 40192) suggested that EPA establish numerical standards, because they allow any treatment, other than impermissible dilution, to be used to comply with the land disposal restrictions.

We find that there is adequate documentation in SW-846 methods 8270, 8315, and 8325 to calculate numerical standards for all but benzaldehyde, 1,3-phenylenediamine, p-toluidine, and 2,4-xylidine. For these constituents we propose to transfer the performance of similar constituents analyzed by method 8270. Thus, we are able to propose numerical standards for all, but one (1,2-phenylenediamine) of the constituents of concern in the K181 wastes.

While we have chosen as the lead option compliance with numerical standards, if these numerical standards are shown in comment to be not achievable or otherwise appropriate, we could be forced to rely on technology based standards alone. Under the technology only approach, all nonwastewaters identified as K181 would be treated by CMBST, and all wastewaters would be treated by either WETOX or CHOXD, followed by CARBN or CMBST.

The proposed treatment standards are presented in the following table.

Proposed Treatment Standards for Constituents in K181				
Constituents of Concern	CAS Number	Wastewater (mg/L)	Nonwastewater (mg/kg)	
Aniline	65-53-3	0.81 *	14 *	
o-Anisidine (2-methoxyaniline)	90-04-0	0.010	0.66	
Azobenzene **	103-33-3	0.010	0.66	
Benzaldehyde **	100-52-7	0.065	4.3	
4-Chloroaniline	106-47-8	0.46 *	16 *	
p-Cresidine	120-71-8	0.010	0.66	
2,4-Dimethylaniline (2,4-xylidine)	95-68-1	0.010	0.66	
1,2-Phenylenediamine	95-54-5	CMBST; or CHOXD fb	CMBST	
		(BIODG or CARBN); or		
		BIODG fb CARBN		
1,3-Phenylenediamine	108-45-2	0.010	0.66	
Toluene-2,4-diamine	95-80-7	0.020	1.30	
p-Toluidine **	106-49-0	0.010	0.66	

<sup>\*</sup> Existing universal treatment standard. No change proposed.

<sup>\*\*</sup> Treatment standards would not be promulgated for this constituent if biodegradation rates are assigned for all constituents based upon structural similarity. See preamble section IV.A.4.

#### 1.0 INTRODUCTION

Resource Conservation and Recovery Act (RCRA) Section 3004(m) specifies that treatment standards must minimize long- and short- term threats to human health and the environment arising from land disposal of hazardous wastes. The U.S. Environmental Protection Agency's (EPA's) general approach for complying with this requirement was promulgated as part of the November 7, 1986 Solvents and Dioxins rule. More recently, EPA has presented its guidance in establishing treatment standards in the Final Best Demonstrated Available Technology (BDAT) Background Document for Quality Assurance/Quality Control Procedures and Methodology, October 1991.

EPA's treatment standards for individual wastes are presented at Title 40, <u>Code of Federal Regulations</u>, Section 268.40 (40 CFR §268.40). For a given waste, a treatment standard specifies (1) the concentration of each constituent in total or TCLP analysis, or (2) a technology which must be used for treating the waste. EPA establishes treatment standards for wastewaters and nonwastewaters, as well as any subgroups which may be appropriate (e.g., "high mercury" or "low mercury" categories for D009 wastes). EPA has also established universal treatment standards for underlying hazardous constituents; these are listed at 40 CFR §268.48.

EPA is proposing Land Disposal Restriction (LDR) treatment standards based on Best Demonstrated Available Technology (BDAT) for the regulation of listed hazardous wastes proposed to be identified in 40 CFR §261.32 as K181. These LDR treatment standards are being proposed in accordance with the amendments to the 1976 RCRA, enacted by the Hazardous and Solid Waste Amendments (HSWA) of November 8, 1984. HSWA amended RCRA to require EPA to promulgate treatment standards for a waste within 6 months after determining it is hazardous [3004(g)(4)].

Compliance with the proposed treatment standards is a prerequisite for land disposal, as defined in 40 CFR Part 268. In 40 CFR §268.44, EPA supplies provisions, that, if met, may justify granting a variance from the applicable treatment standards. In 40 CFR 268.6, EPA

supplies provisions, that, if met, may justify granting waste- and site-specific waivers from the applicable treatment standards in §268.40.

The waste generated during the production of dye and pigment products is proposed to be defined in 40 CFR 261.32 as follows:

K181- Nonwastewaters from the production of dyes and/or pigments (including nonwastewaters commingled at the point of generation with nonwastewaters from other processes) that, at the point of generation, contain mass loadings of any of the constituents identified in  $\S(c)(1)$  of this section that are equal to or greater than the corresponding  $\S(c)(1)$  levels, as determined on a calendar year basis. These wastes would not be hazardous if: (i) the nonwastewaters do not contain annual mass loadings of the constituent identified in  $\S(c)(2)$  of this section at or above the corresponding  $\S(c)(2)$  level; and (ii) the nonwastewaters are disposed in a Subtitle D landfill cell subject to the design criteria in §258.40 or in a Subtitle C landfill cell subject to either §264.301 or §265.301. For the purposes of this listing, dyes and/or pigments production is defined in §(b)(1) of this section. Section (d) of this section describes the process for demonstrating that a facility's nonwastewaters are not K181. This listing does not apply to wastes that are otherwise identified as hazardous under §§261.21-24 and 261.31-33 at the point of generation. Also, the listing does not apply to wastes generated before any annual mass loading limit is met.

This background document provides the Agency's rationale and technical support for developing LDR treatment standards for K181.

# 1.1 Regulatory Background

Section 3001(e)(1) of RCRA requires EPA to determine whether to list as hazardous wastes from the production of 'dyes and pigments.' In June of 1991, EPA entered into a consent decree in a lawsuit filed by the Environmental Defense Fund, et al. (EDF v. Reilly, Civ. No. 89-0598 (D.D.C.), hereinafter referred to as the consent decree). The consent decree as amended sets out a series of deadlines for promulgating RCRA listing decisions, including a requirement to propose a hazardous waste listing determination for certain wastes from the production of dyes and pigments by November 10, 2003 and to promulgate a final decision by February 16, 2003.

There are three major classes of dyes and pigments: azo/benzidine, anthraquinone, and triarylmethane. The consent decree specifies that the listing was to address the azo, monoazo, diazo, triazo, polyazo, azoic, benzidine and pyrazolone categories of the azo/benzidine dye and pigment class; the anthraquinone and perylene categories of the anthraquinone dye and pigment class; and the triarylmethane, and triphenylmethane, categories of the triarylmethane dye and pigment class. The consent decree also specifies that the listing was to address the following types of wastes where they are found: spent catalysts, reactor still overheads, vacuum system condensate, process waters, spent adsorbent, equipment cleaning sludge, product mother liquor, product standardization filter cake, dust collector filter fines, recovery still bottoms, treated wastewater effluent, and wastewater treatment sludge.

EPA initiated an investigation of the azo/benzidine, anthraquinone, and triaryImethane dye and pigment manufacturing industries. On December 22, 1994 (59 FR 66072), EPA proposed to add five wastes (proposed as K162, K163, K164, K165, and K166) generated during the production of dyes and pigments to the lists of hazardous wastes in 40 CFR §261.32. In the 1994 proposed rule, the Agency deferred action on three waste streams. On July 23, 1999 (64 FR 44444), EPA proposed a listing determination for these three wastes, proposing to add two of these wastes (proposed as K167 and K168) to the lists of hazardous wastes in 40 CFR 261.32. Unlike the 1994 proposed rule, EPA included implementation conditions for the wastes proposed in the 1999 rule, such that the wastes would only be hazardous if they contained any of the constituents identified in the applicable list at a concentration equal to or greater than the risk-based concentration level proposed for that constituent.

In the 1999 proposed rule, EPA concurrently proposed a listing determination and land disposal restrictions for the two wastes. In the 1994 proposed rule, EPA did not propose land disposal restrictions for the five wastes. This background document does not affect the scope of prior proposals.

## 1.2 Summary

The LDR program is designed to protect human health and the environment by prohibiting the land disposal of RCRA hazardous wastes unless specific treatment standards are met. In RCRA Section 3004(m), Congress directed the Agency to: "... promulgate ... levels or methods of treatment ... which substantially diminish the toxicity of the waste or ... the likelihood of migration of hazardous constituents ... so that short-term and long-term threats to human health and the environment are minimized." Key provisions of the LDR program require that: (1) treatment standards are met prior to land disposal, (2) treatment is not evaded by long-term storage, (3) actual treatment occurs rather than dilution, (4) record keeping and tracking follow a waste from "cradle to grave" (i.e., generation to disposal), and (5) certification verifies that the specified treatment standards have been met.

As discussed above, EPA may specify a treatment standard for an individual hazardous waste in one of two ways: (1) the concentration of each constituent in total or leachate analysis, or (2) a technology which must be used for treating the waste.

In its treatment standard development of K181 wastes, EPA used, in part, data obtained through its development of universal treatment standards (UTS) at 40 CFR §268.48 as well as its development of treatment standards for "U and P" listed wastes at 40 CFR §268.40. A universal treatment standard is a single concentration limit established for a specific constituent regardless of the waste matrix in which it is present (i.e., the same treatment standard applies to a particular constituent in each waste code in which it is regulated).

## 1.3 Contents of This Document

Section 2.0 discusses the treatment technologies the Agency has designated as "applicable" and "demonstrated" for these wastes, and identifies BDAT for wastewater and nonwastewater forms of these wastes. References are listed in Section 3.0.

The treatment performance data available for the constituents of concern in nonwastewater and wastewater forms of wastes are found in Appendices A and B, respectively.

#### 2.0 TREATMENT STANDARDS FOR DYES AND PIGMENT WASTES

Presented in the sections below are the Agency's determination of applicable and demonstrated technologies and the best demonstrated available technology (BDAT) for treatment of nonwastewater and wastewater forms of K181.

The constituents identified as constituents of concern in these wastes are identified in Table 2-1. Table 2-1 includes the individual constituents proposed as a basis for listing for K181. While additional constituents are present in the wastes, EPA has identified these constituents as presenting the greatest potential risk to human health and the environment. Therefore, EPA will identify methods of treatment which substantially diminish the toxicity of these constituents in particular.

Table 2-1. Constituents Used as the Basis for Listing for K181			
<b>Constituents of Concern</b>	ncern Synomym		
		Number	
Aniline		62-53-3	
o-Anisidine	2-Methoxybenzenamine (o-Aminoanisole)	90-04-0	
Azobenzene *		103-33-3	
Benzaldehyde *		100-52-7	
4-Chloroaniline	4-Chlorobenzenamine	106-47-8	
p-Cresidine	3-Amino-4-methoxytoluene	120-71-8	
2,4-Dimetlylaniline	2,4-Xylidine	95-68-1	
1,2-Phenylenediamine	1,2-Benzenediamine	95-54-5	
1,3-Phenylenediamine	1,3-Benzenediamine	108-45-2	
Toluene-2,4-diamine	2,4-Diaminotoluene	95-80-7	
p-Toluidine *	4-Aminotoluene	106-49-0	

<sup>\*</sup> Treatment standards would not be promulgated for this constituent if biodegradation is assumed. See preamble section IV.A.4.

# 2.1 Determination of LDR Treatment Standards for K181

To establish BDAT, the Agency first identifies which technologies are "applicable" for treatment of the constituents of interest. An applicable technology is one that, in theory, can treat the waste in question (or a similar waste in terms of parameters that affect treatment selection).

Identifying treatment technologies as applicable for treating each constituent is based on evaluation of current waste management practices, current literature sources, field testing, data submitted by equipment manufacturers and industrial concerns, plus engineering judgement of EPA technical staff personnel.

The Agency next determines which of the applicable technologies are "demonstrated" for treatment of the subject wastes. EPA prefers to designate as demonstrated a technology used in a full-scale operation for treatment of the waste of interest or a similar waste. Technologies that are available only at pilot- or bench-scale operations may not be considered demonstrated technologies. EPA may use, in limited circumstances, pilot- and bench-scale data in (1) designating a technology as demonstrated and in (2) developing treatment limits. This would be the case when EPA determines that the performance of pilot- or bench-scale technologies can be optimized to a full-scale operation.

The Agency determines which of the demonstrated technologies is "best" by comparing available treatment performance data from as many systems as possible for the constituents of interest, and determines whether this "best" demonstrated technology is also commercially "available." If the "best" demonstrated technology is "available," then the technology is determined to represent BDAT.

EPA has previously identified technology-specific LDR treatment standards for both wastewaters and nonwastewaters. A description of these treatment standards, including a discussion of other applicable technologies considered and a discussion of why the technologies are effective for treating these wastes, are presented in Sections 2.2 (for nonwastewaters) and 2.3 (for wastewaters).

- 2.2 <u>Identification of Best Demonstrated and Available Technologies (BDAT) for Nonwastewaters</u>
- 2.2.1 Applicable and Demonstrated Technologies

For the organic constituents of concern in K181 wastes, presented in Table 2-1, applicable treatment technologies include those that destroy or reduce the total amount of organic constituents in the waste. The technologies listed below are applicable and have been demonstrated to treat organic constituents in nonwastewater forms of similar hazardous wastes. A thorough discussion of these technologies is presented in U.S. EPA's "Final Best Demonstrated Available Technology (BDAT) Background Document for Universal Standards: Volume A: Universal Standards for Nonwastewater Forms of Listed Hazardous Wastes," July 1994. Only those technologies applicable to the physical and chemical characteristics of K181 are listed below:

- Incineration: This is a destruction technology in which heat is transferred to the waste to destabilize chemical bonds and destroy organic constituents. Offgases (following additional combustion in an afterburner) are fed to a scrubber system for cooling and for removal of entrained particles and acid gas. Typically, scrubber water and ash are generated from incineration. Further discussion of this technology is presented in Section 2.2.2.
- Fuel substitution: Fuel substitution involves using hazardous waste as fuel in industrial furnaces or boilers.
- Solvent extraction: Solvent extraction is a separation and recovery technology that removes organic constituents from a waste by mixing the waste with a solvent that preferentially dissolves and removes the constituents of concern from the waste.
- Critical fluid extraction: This is a separation and recovery technology in which a solvent is brought to its critical state (liquified gas) to extract organic constituents from a waste.
- Pressure filtration: Pressure filtration, also known as sludge dewatering, is a separation and recovery technology used for wastes that contain high concentrations (greater than 1 percent) of suspended solids. It separates particles from a fluid/ particle mixture by passing the fluid through a medium that permits the flow of the fluid but retains particles.
- Thermal drying of biological treatment sludge: This is a destruction technology
  which uses controlled flame combustion or indirect heat transfer to elevate the
  temperature of the waste and, thereby, volatilize organic constituents. Off-gas
  from the dryer is sent to an afterburner to complete combustion of the volatile
  component.
- Thermal desorption: This is a separation and recovery technology in which heat is used to volatilize organic constituents from wastes. The offgas contains steam and volatilized organics.

• Total recycle or reuse: Total recycle or reuse within the same process or an external process eliminates waste generation. As a result of recycling, however, impurities may require removal from the system on a periodic or continuous basis.

Except for total waste recycle and reuse, all of the treatment methods listed above generate additional wastes in liquid or solid form. Such wastes would require additional management, including additional treatment to meet applicable land disposal restriction treatment standards if necessary.

#### 2.2.2 BDAT for K181

For nonwastewater forms of K181, EPA has identified combustion as BDAT. The justification for this determination is as follows:

- Incineration is commercially available, and has been historically used for a variety of wastes.
- Incineration is commonly used for wastes similar in form to nonwastewater forms of K181. Data from the 1999 Biennial Reporting System (BRS) shows that the types of hazardous wastes most likely to be associated with nonwastewater forms of K181 (i.e., organic sludges, biological treatment sludges, still bottoms, and heavy ends) are incinerated.
- In developing its universal treatment standards, the Agency has identified incineration as BDAT for all organic constituents selected for regulation. Many constituents of concern in K181 have universal treatment standards based on incineration and therefore are appropriately treated using incineration.

Incineration was briefly discussed in Section 2.2.1; a more detailed discussion is presented here. This discussion is adapted from U.S. EPA "Final Best Demonstrated Available Technology (BDAT) Background Document for Universal Standards: Volume A: Universal Standards for Nonwastewater Forms of listed Hazardous Wastes," July 1994.

Incineration is a destruction technology in which heat is transferred to the waste to destabilize chemical bonds and destroy hazardous organic constituents. Three incineration technologies are applicable and demonstrated for organics in nonwastewaters: liquid injection, rotary kiln, and fluidized-bed.

In a liquid injection incinerator, liquid wastes are atomized and injected into the incinerator, where additional heat is supplied to destabilize chemical bonds in the presence of air or oxygen. Once the chemical bonds are broken, these constituents react with oxygen to form carbon dioxide and water vapor. Liquid injection is applicable to wastes with low viscosity values, small waste particle size, and low suspended solids content. Since only wastes with low or negligible ash contents are amenable to liquid injection incineration, this technology does not normally generate an ash residual, but does generate a scrubber water residual.

In a rotary kiln incinerator, solid and/or semi-solid wastes are fed into the elevated slope-end of the kiln. The rotation of the kiln mixes the waste with hot gases. Eventually, the waste reaches its ignition temperature, and the waste is converted to gas and ash through volatilization and combustion reactions. Ash is removed from the lower slope-end of the kiln. Combustion gases from the kiln, containing volatilized and partially combusted waste constituents, enter an afterburner for further combustion to complete the destruction of the organic waste constituents. Other wastes may also be injected into the afterburner.

In a fluidized-bed incinerator, solid and/or semi-solid wastes are injected into a fluidized material (generally sand and/or incinerator ash), where they are heated to their ignition temperature. In the incinerator, the waste is converted to gas and ash through volatilization and combustion reactions. Heat energy from the combustion reaction is then transferred back to the fluidized-bed. The velocity of the combustion gases is reduced in a wider space above the bed, known as the "freeboard", allowing larger ash and unburned waste particles to fall back into the bed. Ash is removed periodically both during operation and during bed change-outs.

Combustion gases from incineration are fed into a scrubber system for cooling and removal of any entrained particles and acid gases. In general, with the exception of liquid injection incineration, two residuals are generated by incineration processes: ash and scrubber water.

Not all of the constituents of concern in K181 have previously been shown to be best treated using incineration in EPA's previous development of treatment standards. Specifically,

some constituents do not have any existing treatment standards (i.e., have not previously been studied by EPA). For these compounds without existing treatment standards, EPA expects incineration to treat these constituents adequately. Section 2.2.3 presents justification that all of the constituents of concern in K181 nonwastewaters can be adequately treated by incineration.

# 2.2.3 Ability of Combustion to Treat the Constituents of Concern

Of the organic constituents proposed as the basis for listing K181 nonwastewaters, two have numerical UTS for nonwastewaters (where UTS is based on either incineration) and one has a specified method of treatment for nonwastewaters (where combustion is specified<sup>1</sup>). Treatment standards have not been previously identified for the remaining constituents. These constituents are listed in Table 2-2.

Table 2-2. Existing Treatment Standards for Organic Constituents of Concern in K181 Nonwastewaters				
Constituent of Concern	CAS Number	Existing Standard	Treatment Technology Basis for Standard	
Aniline	62-53-3	14 mg/kg*	Incineration	
o-Anisidine	90-04-0			
Azobenzene**	103-33-3			
Benzaldehyde**	100-52-7			
4-Chloroaniline	106-47-8	16 mg/kg*	Incineration	
p-Cresidine	120-71-8			
2,4-Dimetlylaniline (2,4-Xylidine)	95-68-1			
1,2-Phenylenediamine	95-54-5			
1,3-Phenylenediamine	108-45-2			
Toluene-2,4-diamine	95-80-7	CMBST	Incineration	
p-Toluidine**	106-49-0	CMBST	Incineration	

<sup>--:</sup> No existing standard

These data represent the BDAT for wastes included in previous rulemakings and therefore have been judged to meet the Agency's requirement of BDAT. Although data from the

<sup>\*</sup> Existing universal treatment standard. No change proposed.

<sup>\*\*</sup> Treatment standards would not be promulgated for this constituent if biodegradation rates are assigned for all constituents based upon structural similarity. See preamble section IV.A.4.

<sup>&</sup>lt;sup>1</sup> The specified technology standard, CMBST, is described in 40 CFR §268.42. It includes high temperature organic destruction technologies, such as combustion in incinerators, boilers, or industrial furnaces operated in accordance with specified hazardous waste regulations.

thermal treatment of these constituents in nonwastewater forms of K181 are not available, the thermal destruction technologies can routinely achieve destruction to levels below commonly employed analytical method detection in other wastes as shown in Appendix A; similar performance data were rarely available for constituents without UTS. Based on the results for these constituents with numerical UTS and existing technology based treatment standards, and the evaluation of the remaining chemicals described further in this section, EPA is confident that all the organic constituents of K181 can be adequately treated by incineration to levels below commonly employed analytical method detection limits (i.e., SW-846 Method 8270).

Two measures or indices were used to determine the difficulty of treating each compound via incineration. They are the incinerability index and the thermal stability index. The Agency has utilized each index in past assessments involving incineration of hazardous compounds. The Agency used the incinerability index in EPA's "Best Demonstrated Available Technology (BDAT) Background Document for Newly Listed or Identified Wastes from the Production of Carbamates and Organobromines" (March 2, 1995) while the thermal stability index was cited in EPA's "Guidance on Setting Permit Conditions and Reporting Trial Burn Results: Volume II of the Hazardous Waste Incineration Guidance Series - Appendix D" (January 1989). The following paragraphs discuss these indices in greater detail.

Incinerability Index

The incinerability index is a function of the heat of combustion and the percent concentration of the compound in the waste, given by the following equation:

I = C + 100/H

where

I = incinerability index

C = percent concentration in waste

H = negative heat of combustion of compound (kcal/gram)

The higher the incinerability index, the more difficult it is to destroy the compound. For the calculations presented for K181, concentrations were not used because they are expected to be

less than 1 percent in the subject wastes and therefore were assumed to have negligible effect on the calculation.

## Thermal Stability Index

The thermal stability index (developed by Dellinger and Taylor and described in EPA, 1989) ranks the thermal stability of compounds using several factors, including heat of combustion. The fact that this index uses several parameters in calculating a value to assess ease of combustion may make it more reliable than the incinerability index. The lower the value (closer to one), the more thermally stable the compound and therefore the more difficult to destroy. Based on this approach, it can be concluded that if a compound with a certain ranking is known to be adequately treated by incineration (e.g., 10) then all compounds with values greater than 10 can also be destroyed.

EPA obtained values for the incinerability index and the thermal stability index for as many of the constituents in Table 2-3 as available. The constituents of concern identified to be proposed as the basis of the listing are shaded. In addition Table 2-3 contains the thermal stability index and the incinerability index for structurally similar substances that were evaluated as potential K181 constituents.

Table 2-3. Combustion Indices for Organic Constituents Evaluated				
Constituent of Concern	CAS Number	Negative Heat of Combustion A (kcal/g)  Incinerability Index B		Thermal Stability Index Rank
Aniline E	62-53-3	8.71	11.5	46-50
o-Anisidine / 2-methoxyaniline	90-04-0	7.75	12.9	
Azobenzene **	103-33-3	8.48	11.8	
Benzaldehyde **	100-52-7			
Benzidine	92-87-5	8.47	11.8	60-64
4-Chloroaniline <sup>E</sup>	106-47-8	6.0	16.7	37
Chloroform D	67-66-3	0.75	133	195
p-C residine / 3-amino-4-methoxytoluene	120-71-8			
p-Cresol / 4-methylphenol <sup>E</sup>	106-44-5	8.18	12.2	104-105

Constituent of Concern	CAS Number	Negative Heat of Combustion <sup>A</sup> (kcal/g)	Incinerability Index <sup>B</sup>	Thermal Stability Index Rank
3,3'-Dichlorobenzidine	91-94-1			67
3,3'-Dimethoxybenzidine	119-90-4			250
N,N-Dimethylaniline	121-69-7			
3'3'-Dimethylbenzidine	119-93-7	4.54	22.0	78
Diphenylamine <sup>E</sup>	122-39-4	9.07	11.0	42-44
Formaldehyde	50-00-0	4.55	22.0	46-50
Methanol <sup>E</sup>	67-56-1	5.42	18.5	
Naphthalene <sup>E</sup>	91-20-3	9.6	10.4	5
5-Nitro-o-anisidine / 2-methoxy-5-nitrobenzamine	99-59-2			
5-Nitro-o-toluidine / 2-amino-4-nitrotoluene <sup>E</sup>	99-55-8	5.98	16.7	166-167
Phenol <sup>E</sup>	108-95-2	7.76	12.9	100-101
1,2-Phenylenediamine / 2-aminoaniline	95-54-5	7.83	12.3	57-59
1,3-Phenylenediamine / 3 -aminoaniline	108-45-2	7.80	12.8	57-59
1.4-Phenylenediamine / 4-aminoaniline	106-50-3	7.76	12.9	57-59
Toluene-2,4-diamine	95-80-7			69-67
o-Toluidine / 2-aminotoluene	95-53-4	9.00	11.1	
p-Toluidine / 4-aminotoluene **	106-49-0	9.05	11.0	
2,4-Xylidine / 2,4-dimethylaniline	95-68-1			

A. The heat of combustion in kcal/g was calculated by dividing the heat of combustion in kcal/mol by the molecular weight of the compound. The heats of combustion were taken from the National Institute of Standards and Technology "Chemistry Webbook" at http://webbook.nist.gov/chemistry.

B. Incinerability Index (I) = C + 100/H, where C is equal to the constituent's percent concentration in the waste (assumed to be negligible) and H is the negative heat of combustion in kcal/g. Constituents with higher incinerability index values are more difficult to treat.

C. The constituents with lower thermal stability index values (closest to 1) are more stable and therefore are more difficult to treat. From EPA, "Guidance on Setting Permit Conditions and Reporting Trial Burn Results, volume 2 of the Hazardous Waste Incineration Guidance Series," June 1989 (EPA 625 6-89 019), Appendix D.

D. Not one of the constituents of concern in K181, but is included in this table for purposes of comparison.

E. Constituent has existing numerical UTS.

<sup>--:</sup> Index/Rank/Data not available.

\*\* Treatment standards would not be promulgated for this constituent if biodegradation rates are assigned for all constituents based upon structural similarity. See preamble section IV.A.4.

To use the available data, the Agency has taken a two-fold approach to addressing the treatability of compounds without UTS. The first approach involves using the thermal stability in determining the treatability of the constituents of concern and is most appropriate for constituents with index values. The second approach involves dividing the constituents without UTS into groups based on physical and chemical similarity to compounds with UTS and is most appropriate for assessing the incinerability of non-UTS constituents without index values.

The first approach uses the fact that the constituents of concern have a thermal stability indexes indicate that they would be no more difficult to combust than those substances for which incineration has been demonstrated to provide destruction. For example, naphthalene with a thermal stability index rank of five (5) is expected to be the one of the most difficult organic compounds to destroy via incineration. The UTS for naphthalene was developed using incineration as BDAT, with data (in Appendix A) showing the constituent was not detected in the treated waste. Therefore, it can be expected that all of the remaining less stable compounds will be sufficiently destroyed through incineration. Table 2-3 shows that the remaining compounds have thermal stability indices greater than 5 (i.e., greater than naphthalene), and therefore would be less stable, and easier to treat, than naphthalene.

The same logic can be applied using the incinerability index. The higher the incinerability index, the more difficult the compound is to treat via incineration. For this comparison, data for chloroform was used (even though it is not a constituent of concern in K181 wastes). The UTS for chloroform was established using incineration as BDAT, and Appendix A shows that chloroform can be treated to below analytical detection using incineration. Since chloroform has the highest incinerability index (133), it can be expected that all compounds with lower incinerability index values can be destroyed via combustion. The Incinerability index of o-anisidine and azobenzene are in range of the other constituents known to be treated via combustion.

Table 2-3 shows that three of the constituents of concern still lack data for comparison. These compounds are benzaldehyde, p-cresidine, and 2,4-dimethylaniline (2,4-xylidine). The second approach involves grouping similar compounds and assuming that compounds within each group are of similar thermal stability. This is particularly useful for evaluating the constituents without any combustion index value. If similar chemical structures and chemical and physical properties are exhibited by the constituents in each treatability group, incineration should be able to destabilize and destroy each of the compounds in a similar fashion. This approach relies on the fact that incineration or fuel substitution is the BDAT for each of the compounds with UTS or technology based standards identified as constituents of concern in K181 (EPA's "Final Best Demonstrated Available Technology (BDAT) Background Document for Universal Standards Volume A: Universal Standards for Nonwastewater Forms of Listed Hazardous Wastes", July 1994). The treatability groups that were developed based on similar chemical structure are presented in Table 2-4.

Table 2-4. Treatability Groups for Constituents of Concern in Nonwastewaters				
Treatability Group(A)	Constituents of With NWW UTS	Constituents with CMBST as Specified NWW Technology	Constituents of Concern Without NWW Standards	
Aryl amine compounds	Aniline (I) 4-Chloroaniline (I)	Toluene-2,4-diamine (I) p-Toluidine (I)	o-Anisidine (I) Azobenzene (I) p-Cresidine 1,2-Phenylenediamine (I) 1,3-Phenylenediamine (I) 2,4-Xylidine	
Oxygenated Compounds	o-Cresol (I) Phenol (I) Methanol	Formaldehyde (I)	Benzaldehyde	

A. These constituent groupings are intended to apply only in evaluating the similarity of properties as applied to nonwastewaters.

For the first treatability group (aryl amine compounds), EPA believes these compounds have sufficiently similar structures and functional groups, and therefore believes that incineration can be applied to the remaining aryl amine compounds for which standards need to be developed. Table 2-3 shows that the thermal stability index values range from 37 to 69 for all but one of compounds in this treatability group, and that substance has a significantly higher index indicating that it is more easily destroyed. Due to the sufficiently narrow range of index values,

<sup>(</sup>I) Indicates the constituent has a thermal stability index value or an incinerability index value as indicated in Table 2-3.

and the similar structural and physical properties exhibited throughout this treatability group, EPA is confident that incineration can be used to treat the remaining constituents in this treatability group. All four of the five of the constituents lacking thermal stability data are in this group.

Similar comparisons can be made for one of the remaining substance, benzaldehyde, for which there is no existing treatment standard. Benzaldehyde would be expected to have combustion properties similar to o-cresol. Therefore, we are confident that it also can be treated by incineration.

While there is a lack of data regarding whether incineration is a documented destruction technology for all of the compounds under evaluation, incineration can still be expected to reduce or destroy these compounds in the waste matrix. As noted before, incineration is demonstrated and applicable to a wide range of organic compounds. Second, these compounds have some similarities to the other treatability groups identified above (i.e., they contain oxygen, nitrogen, and carbon), and so are also expected to be adequately treated using incineration.

In conclusion, the Agency believes that the BDAT of incineration can reasonably be transferred to all nonwastewater constituents without numerical UTS based on (1) the thermal stability index ranking system and incinerability index (if the most difficult to treat constituents can be destroyed via incineration, then all less stable constituents can also be destroyed); and (2) similar chemical structures and chemical and physical properties that are exhibited by the constituents in each treatability group (incineration should be able to destabilize and destroy each of the compounds in a similar fashion).

# 2.3 <u>Identification of Best Demonstrated and Available Technologies (BDAT) for</u> Wastewaters

# 2.3.1 Applicable and Demonstrated Technologies

The constituents of concern in these wastes were presented in Table 2-1. Applicable treatment technologies are those that destroy or reduce the total amount of organic constituents in

the waste. The technologies listed below are applicable and have been demonstrated to treat organic constituents in wastewater forms of other hazardous wastes. A thorough discussion of these technologies is presented in U.S. EPA's "Final Best Demonstrated Available Technology (BDAT) Background Document for Universal Standards: Volume B: Universal Standards for Wastewater Forms of Listed Hazardous Wastes" (1994). Only those technologies applicable to the physical and chemical characteristics of K181 are listed below:

- Biological treatment (including aerobic fixed film, aerobic lagoon, activated sludge, anaerobic fixed film, rotating biological contactor, sequential batch reactor, and trickling filter technologies);
- Carbon adsorption treatment (including activated carbon and granular activated carbon technologies);
- Chemically assisted clarification treatment (including chemical precipitation technology);
- Chemical oxidation;
- PACT® treatment (including powdered activated carbon addition to activated sludge and biological granular activated carbon technologies);
- Reverse osmosis treatment;
- Solvent extraction treatment (including liquid/liquid extraction);
- Stripping treatment (including steam stripping and air stripping technologies);
- Wet air oxidation treatment (including supercritical oxidation technology); and
- Total recycle or reuse.

Each of these technologies are discussed briefly below, with additional discussion in Section 2.3.3 for chemical oxidation, wet air oxidation, and carbon adsorption.

The concentrations and type(s) of constituents present in the waste generally determine which technology is most applicable. Carbon adsorption, for example, is often used as a polishing step following primary treatment by biological treatment, solvent extraction, or wet air oxidation. Typically, carbon adsorption is applicable for treatment of wastewaters containing

less than 0.1% total organic constituents. Wet air oxidation, PACT® treatment, biological treatment, and solvent extraction are generally applicable for treatment of wastewaters containing up to 1% total organic constituents. Some K181 wastewaters may not be treated effectively by biological treatment or PACT® if they contain constituents that are too toxic to support biomass growth.

## Biological Treatment

Biological treatment is a destruction technology that biodegrades hazardous organic constituents in wastewaters. This technology generates two treatment residuals: a treated effluent and a waste biosludge. Waste biosludge may be land disposed without further treatment if it meets the applicable BDAT treatment standards for regulated constituents.

# Carbon Adsorption

Carbon adsorption is a separation technology that selectively adsorbs organic constituents in wastewaters onto activated carbon. This technology generates two treatment residuals: a treated effluent and spent activated carbon. The spent activated carbon may be reactivated, recycled, incinerated, or land disposed without further treatment if it meets the applicable BDAT treatment standards for regulated constituents.

#### Chemically Assisted Clarification

Chemically assisted clarification, including chemical precipitation, is a separation technology that removes organic and inorganic constituents from wastewater by the addition of chemicals that cause precipitates to form. The solids formed are then separated from the waste water by settling, clarification, and/or polishing filtration. This technology generates two treatment residuals: treated wastewater effluent and separated solid precipitate. The solid precipitate may be land disposed without further treatment if it meets the applicable BDAT treatment standards for the regulated constituents in nonwastewater forms of waste.

#### Chemical Oxidation

Chemical oxidation is a destruction technology that oxidizes inorganic cyanide, some dissolved organic compounds, and sulfides to yield carbon dioxide, water, salts, simple organic acids, and sulfates. This technology generates one treatment residual: treated effluent.

#### PACT® Treatment

PACT® treatment combines carbon adsorption and biological treatment to biodegrade hazardous organic constituents and selectively adsorb them onto powdered activated carbon. This technology generates two treatment residuals: a treated effluent and spent carbon/biosludge. The spent carbon is often regenerated and recycled to the process or incinerated. PACT® technology has been applied to the treatment of wastewaters from the textile and dyes industries (U.S. Filter/Zimpro Products; www.zimpro.com).

#### Reverse Osmosis

Reverse osmosis is a separation technology that removes dissolved organics (usually salts) from a wastewater by filtering the waste water through a semipermeable membrane at a pressure greater than the osmotic pressure caused by the dissolved organics in the wastewater. This technology generates two treatment residuals: the treated effluent and the concentrated organic salt materials which do not pass through the membrane.

# Solvent Extraction

Solvent extraction is a separation technology that removes organic compounds from a waste due to greater constituent solubility in a solvent phase than in the waste phase. This technology generates two residuals: a treated waste residual and an extract. The extract may be

recycled or treated by incineration. The treated residual may need to undergo further treatment for metals, such as stabilization. Recovered solvent may be recycled back into the process.

# Stripping Treatment

Stripping treatment is a separation technology in which volatile organic constituents in a liquid waste are physically transferred to a flowing gas or vapor. In steam stripping, steam contacts the waste, strips the volatile organics, and carries them to a condenser where the mixture of organic vapors and steam is condensed and collected in an accumulator tank. In air stripping, air contacts the waste and strips the volatile organic constituents. Stripping generates one treatment residual: treated effluent. Emissions from stripping treatment may require further treatment.

#### Wet Air Oxidation

Wet air oxidation is a destruction technology that oxidizes hazardous organic constituents in wastes under pressure at elevated temperatures in the presence of dissolved oxygen. This technology is applicable for wastes comprised primarily of water and with up to 10% total organic constituents. Wet air oxidation generates one treatment residual: treated effluent. The treated effluent may require further treatment for hazardous organic constituents by carbon adsorption or PACT® treatment. Trapped air emissions from wet air oxidation may also require further treatment.

## Total Recycle or Reuse

Total recycle or reuse within the same process or an external process eliminates waste generation. As a result of recycling, however, impurities may require removal from the system on a periodic or continuous basis.

#### 2.3.2 BDAT for Wastewater Forms of K181

For wastewater forms of K181, EPA has identified the following treatment train as BDAT: wet air oxidation or chemical oxidation, followed by carbon adsorption. Alternatively, treatment using combustion can also be used. While a single technology, combustion, was shown to be BDAT for a wide variety of constituents in nonwastewaters, BDAT differs for organic constituents in wastewaters according to the chemical's physical and chemical properties (such as vapor pressure and solubility). The justification for determining that this treatment train as BDAT for wastewater forms of K181 is as follows:

- Chemical oxidation, wet air oxidation, and carbon adsorption are used in full-scale, operating systems to treat organics in wastewaters, including dye or pigment industry wastewaters. This is discussed further in this section.
- Two of the treatment trains include an oxidation step followed by an adsorption step. As shown in the next section, this train has the ability to treat a wide range of organic constituents of varying properties.
- As discussed in Section 2.2, combustion is being proposed as BDAT for nonwastewater forms of K181. The same constituents of concern are expected to be present in wastewater forms of these wastes, and liquids such as wastewater can be adequately treated using technologies such as liquid injection incineration. Therefore, combustion is being proposed as one alternative to treating K181 wastewaters.

Not all of the constituents of concern in K181 have previously been shown to be best treated using the above treatment trains in EPA's previous development of treatment standards. Specifically, other constituents do not have any treatment standards (i.e., have not previously been studied by EPA), while others have treatment standards based on different technologies (most often activated sludge or biological treatment). Section 2.3.3 below presents EPA's justification that all of the constituents of concern in K181 can be adequately treated by the above treatment train.

#### 2.3.3 Ability of Proposed Train to Treat the Constituents of Concern

Of the organic constituents proposed as constituents of concern K181, two chemicals have UTS (for wastewaters), one has a technology-specific standard, and the remaining compounds do not have any existing treatment standard. The constituents are shaded in Table 2-

5. In addition Table 2-5 contains the technology standards or technical basis for structurally similar substances that were evaluated as potential K181 constituents.

Table 2-5. Existing Treatment Standards for Constituents Evaluated in K181 Wastewaters			
Constituent of Concern	CAS	UTS WW	Technology Standard or Technical Basis for
	Number	(mg/L)	UTS
2-Aminoanthroquinone	117-79-3		
Aniline *	65-53-3	0.81	Liquid-liquid extraction plus steam stripping plus
			activated carbon
o-Anisidine (2-methoxyaniline)	90-04-0		
Azobenzene **	103-33-3		
Benzaldehyde **	100-52-7		
Benzidine	92-87-5	(T)	(WETOX or CHOXD) fb CARBN; or CMBST
4-Chloroaniline *	106-47-8	0.46	WETOX fb CARBN
p-Cresidine	120-71-8		
p-Cresol	106-44-5	0.77	Activated sludge
o-Dichlorobenzene	95-50-1	0.088	Biological treatment
3,3'-Dichlorobenzidine	91-94-1	(T)	(WETOX or CHOXD) fb CARBN; or CMBST
3,3'-Dimethoxybenzidine	119-90-4	(T)	(WETOX or CHOXD) fb CARBN; or CMBST
2,4-Dimethylaniline (2,4-Xylidine)	95-68-1		
N,N-Dimethylaniline	121-69-7		
3,3'-Dimethylbenzidine	119-93-7	(T)	(WETOX or CHOXD) fb CARBN; or CMBST
Diphenylamine	122-39-4	0.92	Activated sludge
Formaldehyde	50-00-0	(T)	(WETOX or CHOXD) fb CARBN; or CMBST
Methanol	67-56-1	5.6	CARBN
4,4'-Methylenedianiline	101-77-9		
Naphthalene	91-20-3	0.059	Biological treatment
5-Nitro-ortho-anisidine	99-59-2		
5-Nitro-ortho-toluidine	99-55-8	0.32	CARBN
Phenol	108-95-2	0.039	Biological treatment
1,2-Phenylenediamine	95-54-5		
1,3-Phenylenediamine	108-45-2		
1,4-Phenylenediamine	106-50-3		
Tetramethyldiaminobenzophone	90-94-8		
Toluene-2,4-diamine	95-80-7	(T)	CARBN; CMBST
o-Toluidine	95-53-4	(T)	CMBST; or CHOXD fb (BIODG or CARBN); or BIODG fb CARBN
p-Toluidine **	106-49-0	(T)	CMBST; or CHOXD fb (BIODG or CARBN); or BIODG fb CARBN

<sup>\*</sup> Existing universal treatment standard. No change proposed.

The technologies identified as 'best' depends on the compound being treated. Many of the volatile compounds are best treated using steam stripping. Other compounds have UTS

<sup>\*\*</sup> Treatment standards would not be promulgated for this constituent if biodegradation rates are assigned for all constituents based upon structural similarity. See preamble section IV.A.4.

developed based on the performance of some type of biological activity system (e.g., activated sludge). Finally, EPA previously determined that other constituents are best treated using oxidation and carbon adsorption in series. In developing treatment standards for K181 wastewaters, EPA considered all of the technologies listed in Table 2-5, other applicable technologies described in Section 2.3.1, and technologies described in Section 2.3.1 that are used by domestic dye and pigment manufacturers as described in public comments to the 1994 proposed rule. The technologies identified from public comments are presented in Table 2-6.

Table 2-6. Demonstrated Technologies for Dyes and Pigments Wastewaters		
Technology	Examples of Companies Using Technology	
Biological treatment	Clariant (Martin, SC) produced azo dyes, anthraquinone dyes, and azo pigments. Wastewater was treated in an aerated, activated sludge system.	
	Hoechst Celanese (Coventry, RI) produced azo dyes and azo pigments. Wastewaters from azo dye production were treated using chlorine addition, then mixed with pigment wastewaters. The wastewaters were sent through neutralization and equalization, and to aerated biological treatment. Sludge was removed by clarifiers.	
Carbon adsorption	Ceiba-Gegy (St. Gabriel, LA), a dye manufacturer, treated wastewater in a treatment train that includes activated carbon. The activated carbon was regenerated offsite or onsite.	
PACT®	Crompton & Knowles (Gibraltor, PA), an azo dye manufacturer, treated diluted process wastewaters through initial neutralization and equalization.  PACT® treatment (carbon adsorption in conjunction with biological treatment) was conducted in conjunction with aeration and mixing. The solids were removed by adding polymer followed by clarification. The treated water was permitted for surface water discharge.	

Table 2-6. Demonstrated Technologies for Dyes and Pigments Wastewaters		
Technology	Examples of Companies Using Technology	
Steam stripping	Wastewater generated by Morton (Paterson NJ), an azo and anthraquinone dye manufacturer, was sent to neutralization and equalization tanks then to a steam stripper. Vapors from the stream stripper were incinerated. The treated water was permitted for discharge to a POTW.	
	Hilton Davis (Cincinnati, OH), an azo dye and pigment manufacturer, used air stripping in its wastewater treatment train prior to permitted discharge to a POTW.	
Recycle/reuse	Hoechst Celanese (Mount Holly, NC) reused wastewater from azo dye production. The washwaters from equipment rinsing was incorporated into the final product.	

Source: Public comments to 59 FR 66072 (Dec. 22,1994), Docket No. F-94-DPLP-FFFFF. Comment numbers 00023 (Crompton and Knowles, pages 19 to 22); 00022 (Morton, pages 2 to 4); 00016 (Hilton Davis, pages 13 to 14); 00021 (Hoechst Celanese, pages 30 to 32); 00033 (Clariant); 00029 (Ciba-Geigy, pages 2 to 3).

Stripping processes rely on the transfer of contaminants from the aqueous phase to the gas phase. Additionally, the contaminants that are transferred to the resulting gas must be further treated or destroyed prior to release to the environment. For these reasons, steam stripping is not an appropriate treatment technology for the many nonvolatile components potentially present in K181 wastewaters and was not considered further in the development of BDAT for these wastes. Systems relying on biological activity (such as biological treatment, PACT® or activated sludge treatment) are advantageous because the system is flexible enough to treat a wide variety of organic constituents, and does so by destruction (rather than removal to another medium). A disadvantage of this treatment is that the performance of all constituents included as constituents of concern is not known. Specifically, it is possible that some of the constituents would be toxic to the organisms in the biological treatment system at certain concentrations, and EPA has no data regarding what this concentration would be. If a control influent concentration were identified for each constituent, treatment unit operators could not necessarily monitor the levels

of constituents in the influent if analytical measurement at very low levels were necessary. For these reasons, EPA is not proposing that biological treatment be proposed as a treatment standard for these wastes. These reasons primarily relate to uncertainty in the performance of biological treatment in treating these constituents.

General Performance of Chemical Oxidation, Wet Air Oxidation, and Carbon Adsorption

Both wet air oxidation and chemical oxidation provide treatment by destroying hazardous constituents in wastewaters. These technologies are part of the treatment standards for many U and P wastewaters (e.g., many of the technology-based treatment standards in Table 2-5 include these technologies as part of the treatment train). As discussed in Section 2.3.1, wet air oxidation involves the mixing of oxygen with waste at elevated temperature, converting hydrocarbons to carbon dioxide and water (a process with some similarities to combustion). Chemical oxidation uses oxygen or stronger oxidants (such as chlorine or ozone) to similarly convert hydrocarbons to oxidation products. These processes are effective in reducing indicator parameters (such as chemical oxygen demand) when measurement of individual compounds is not, or cannot, be performed (Stephenson, 1993). Carbon adsorption is capable of treating a wide variety of organic contaminants, both volatile and nonvolatile.

As discussed in Section 2.2.3, K181 nonwastewaters can be adequately treated by incineration. Because wet air oxidation similarly involves oxidation of these components at elevated temperatures, EPA expects the technology to treat many of the K181 contaminants

(notwithstanding the obvious difference of the physical state of the waste between wet air oxidation and incineration).

Several vendors were identified that currently perform wet air oxidation, chemical oxidation, and/or carbon adsorption on wastewaters. These companies include: US Filter/Zimpro, Calgon Carbon Corporation, Vulcan Peroxidation Systems, Inc., Sumas, Mantech Environmental Corporation, Stablex Services, Van Waters & Rogers, and Cameron Environmental. Vulcan Peroxidation Systems, Inc. has applied their Perox-Pure chemical oxidation process to forty full-scale industrial applications (Yang, 1998). Three other companies' services are discussed in detail below.

US Filter/Zimpro (http://www.zimpro.com) uses a wet air oxidation process in which oxidation reactions occur at moderated temperatures of 275°F to 600°F and at pressures from 150 to 3,000 pounds per square inch. This process can convert organic contaminants to water, carbon dioxide, and biodegradable short chain organic acids. The Calgon Carbon Corporation (http://www.calgoncarbon.com) uses chemical oxidation in series with carbon adsorption. Their chemical oxidation system incorporates the generation of hydroxyl radicals (OH•) for the destruction of organic compounds, generated from hydrogen peroxide activated by ultraviolet (UV) light. Rates of reaction of organic pollutants with hydroxyl radicals are often orders of magnitude faster than rates involving ozone, or hydrogen peroxide only, and can be carried out at ambient temperature and pressure. Such systems have been commercially available since the early 1980s. Finally, Ebara Research Company (Japan) has identified an oxidation technology that includes oxidation using air and hydrogen peroxide. Inorganic chlorides are added and the resulting solution is heated and charged with electric current. The electricity results in the

electrolytic oxidation of contaminants. This process is in development phase and has not been commercially applied (Chemical Engineering, 2000).

Wet air oxidation is used for high strength wastewater steams prior to final biological treatment. Specific examples include: ethylene and refinery spent caustic liquors, high strength petrochemical wastewater streams, and coke oven gas liquors. The types of contaminants destroyed include chlorinated alkenes, aromatics, phenols, PAHs, PCBs, and alcohols, with concentrations ranging from a few ppb to several hundred ppm.

In addition, Kirk-Othmer (1993) states that wet air oxidation and chemical oxidation using chlorine, bleach, ozone, and hydrogen peroxide are demonstrated methods to treat wastewaters from dye manufacturing. The subject of dyes wastewater treatment techniques has been well-studied in the literature. Three recent papers have discussed chemical oxidation, specifically with the use of hydroxyl radicals (OH•) generated from ultraviolet light and hydrogen peroxide (Kang, 1999, Yang, 1998, and Ruppert, 1994). Indicator parameters such as total organic carbon, chemical oxygen demand, and color are reduced from 90 to 100 percent for both azo and triarylmethane dye classes. In addition, dye manufacturing wastewater was oxidized using UV light, hydrogen peroxide, and ferrous ions (known as the advanced oxidation process). It was concluded that this oxidation process reduced color and COD by nearly 100 percent. All three of these papers discussed results at the bench-scale level.

Carbon adsorption is also used for removing organic contaminants from dye wastewaters.

As identified in Table 2-6, the technology is used at one domestic facility.

It is expected that the physical/chemical properties of the currently treated dye wastewaters will overlap with the physical/chemical properties of K181 wastewaters. The aforementioned examples of commercial oxidation along with the Kirk-Othmer discussion show that oxidation is a demonstrated and effective treatment process for a variety of organic wastewaters including contaminants or chemical classes specific to K181. Therefore, the technologies of oxidation and carbon adsorption could be applied or optimized to treat contaminants in wastewater forms of K181.

Treatment Data for Chemical Oxidation, Wet Air Oxidation, and Carbon Adsorption

EPA acknowledges that it does not have performance data for many of the constituents of concern in K181 using these technologies. Available data regarding the removal efficiency for chemical oxidation and wet air oxidation are presented in Appendix B, for six of the organic constituents of concern. For the oxidation technologies alone, all constituents with data exhibit significant percent reduction standards of greater than or equal to 80 percent. Similarly, available data on the removal efficiency for carbon adsorption are presented in Appendix B, for aniline and 4-chloroaniline. EPA evaluated these data to assess the effectiveness of the proposed treatment train.

In regard to the remaining constituents, some are sufficiently similar in structure and properties to constituents with data so that the performance data for oxidation can be extrapolated. This was generally assessed using the treatability groups defined for

nonwastewaters in Section 2.2.3. The uncertainty associated with this analysis is high because of the lack of data for many of the compounds, particularly for the other aniline derivatives.

For the carbon adsorption technology, there are limited data available for the constituent aniline.

#### Conclusion

The organic constituents of concern in wastewater forms of K181 have diverse physical and chemical properties. There are many wastewater treatment technologies on the market, some of which are extremely specific or limited in the types of constituents which can be treated. Wet air oxidation and chemical oxidation are technologies which are shown to have been used for a variety of wastes and contaminants, including some of those contaminants expected to be present in K181 wastewaters.

EPA is confident that wet air oxidation or chemical oxidation is effective in treating many of the contaminants of K181 wastewaters, as evidenced by the reduction of indicator parameters such as chemical oxygen demand, and the documented removal of specific contaminants in EPA National Risk Management Research Laboratory (NRMRL) Treatability Data Base data. However, the Agency acknowledges that the effectiveness of these processes cannot be accurately judged on a constituent level basis for every contaminant. To better ensure effective treatment, EPA is proposing the K181 wastewater treatment train to also include a carbon adsorption step. Carbon adsorption is intended to remove those contaminants left untreated by the oxidation step, as well as any oxidation by-products.

A third alternative treatment technique, incineration, is expected to result in near-complete destruction (i.e., to below analytical detection) for all constituents of concern in K181. This was shown in Section 2.2.3 for nonwastewaters, and can be equally applied to wastewaters.

Available performance data regarding chemical oxidation, wet air oxidation, and carbon adsorption are presented in Appendix B. Data are only available for two of the constituents of concern in K181, leading to some uncertainty regarding the ability of this treatment train in effectively treating all the constituents of concern. However, the data that are available show very good performance, often to below analytical method detection limits.

These technologies are commercially available and in use for treating a variety of constituents in wastewaters including the treatment of dye industry wastewater. EPA expects that their use can be optimized, if necessary, to treat the specific contaminants in K181 wastewaters.

# 2.4 Proposed Numerical Treatment Standards

Numerical treatment standards have been promulgated for only two (aniline and 2-chloroaniline) of the organic constituents of concern. One (toluene-2,4-diamine) has existing technology based treatment requirements. Commenters to the July 23, 1999 listing proposal (64 FR 40192) suggested that EPA establish numerical standards, because they allow any treatment, other than impermissible dilution, to be used to comply with the land disposal restrictions. We used the following assumptions in developing possible numerical treatment standards:

- For nonwastewaters, EPA has determined that incineration can be used to destroy all constituents of concern in the subject wastes, as described in Section 2.2 of this report.
- For wastewaters, EPA is assuming for purposes of numerical treatment standard development that application of the BDAT would result in none of the constituents being present at detectable levels, as described in Section 2.3 of this report.
- It is assumed for constituents that lack performance documentation, that they exhibit similar performance to structurally similar constituents which have been evaluated.

EPA does not have data demonstrating what the detection limit would be in the actual waste matrixes. However, EPA has data resulting from the analysis of various solid wastes, as well as laboratory control samples representing a clean sand matrix from method validation efforts. Although neither material duplicates an incineration residue, EPA believes that the incineration residue would more closely approximate the clean sand matrix than the wastes from dye manufacturing, because many of the organic contaminants present in the dye wastes (which would potentially result in matrix interference and elevated detection limits) would be absent following incineration. For wastewaters, EPA believes that the treated wastewater residue would more closely approximate the reagent water matrix than the wastes from dye manufacturing for

similar reasons. Thus, we have relied upon the performance demonstrations of SW-846 Method 8315 (HPLC), SW-846 Method 8321 (HPLC/MS), and SW-846 Method 8270 (GC/MS). From the reported detection limits of these methods, we have calculated numerical standards.

SW-846 Method 8315A Determination of Carbonyl Compounds by High Performance Liquid Chromatography (HPLC) has documented performance for formaldehyde which is transferred to benzaldehyde. Method 8270C Semivolatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS) references estimated quantitation levels for o-anisidine, p-cresidine, o-toluidine, and 1,4-phenylenediamine of 0.010 mg/L or 0.66 mg/kg. We propose to transfer this performance level to the remainder of the constituents of concern that lack existing numerical treatment standards. Significant improvements have been made in instrument sensitivity and chromatographic column performance since Method 8270 was first developed. Therefore, we believe that these numerical standards may now be readily measured by the majority of laboratories equipped to perform such analyses.

For 1,2-phenylenediamine, past method performance evaluations had difficulty in achieving reliable recovery from aqueous matrixes and precise measurements. (See 63 FR 47411, September 4, 1998.) Therefore, for this constituent we propose that wastewaters be treated by CMBST; or CHOXD fb (BIODG or CARBN); or BIODG fb CARBN, and all nonwastewaters would be treated by CMBST. If data adequate for the development of a numerical standard is presented in comment, the Agency may promulgate a numerical standard as an alternative, or as the treatment requirement.

The proposed numerical treatment standards are provided in Table 2-7.

Table 2-7. Proposed Numerical Treatment Standards for Constituents in K181					
Constituent of Concern	CAS	ww	NWW	Source	
	Number	(mg/L)	(mg/kg)		
Aniline *	65-53-3	0.81	14 mg/kg	Existing UTS	
o-Anisidine (2-methoxyaniline)	90-04-0	0.010	0.66	8270	
Azobenzene **	103-33-3	0.010	0.66	8270/ 1,2-	
				diphenylhydrazine	
Benzaldehyde **	100-52-7	0.065	4.3	Transfer formaldehyde	
4-Chloroaniline *	106-47-8	0.46	16 mg/kg	Existing UTS	
p-Cresidine	120-71-8	0.010	0.66	8270	
2,4-Dimethylaniline (2,4-Xylidine)	95-68-1	0.010	0.66	8270 Transfer	
1,2-Phenylenediamine	95-54-5	***	***		
1,3-Phenylenediamine	108-45-2	0.010	0.66	8270 Transfer	
Toluene-2,4-diamine	95-80-7	0.020	1.30	8270	
p-Toluidine	106-49-0	0.010	0.66	8270 Transfer	

<sup>\*</sup> Existing universal treatment standard. No change proposed.

## 2.5 Alternative Technology Based Treatment Standards

Wastes that are identified as K181 must be treated before disposal. While we have chosen as the lead option compliance with numerical standards, if these numerical standards are shown in comment to be not achievable or otherwise appropriate, we could be forced to rely on technology based standards alone. Under the technology only approach, all wastewaters identified as K181 would be treated by (WETOX or CHOXD) followed by CARBN or CMBST, and all nonwastewaters would be treated by CMBST.

<sup>\*\*</sup> Treatment standards would not be promulgated for this constituent if biodegradation rates are assigned for all constituents based upon structural similarity. See preamble section IV.A.4.

<sup>\*\*\*</sup> Proposed technology based standards

## 3.0 REFERENCES

Chemical Engineering. Chementator. "Electrolytic Oxidation Removes Organic Pollutants from Water." May 2000. Page 17.

Chowdhury, Jayadev. "A Catalytic Oxidizer for Treating Acrylate Wastes." Chemical Engineering 99(9). September 1992. Page 25.

Kang, Shyh-Fang, et. al. "Peroxidation Treatment of Dye Manufacturing Wastewater in the Presence of Ultraviolet Light and Ferrous Ions." Journal of Hazardous Materials. Volume 65. Number 3. March 19, 1999. Page. 317.

Kirk-Othmer Encyclopedia of Chemical Technology. "Dyes and Dye Intermediates." John Wiley and Sons. Fourth Edition. Volume 8 (1993).

National Institute of Standards and Technology, "Chemistry Webbook," at http://webbook.nist.gov/chemistry.

Ruppert, Gerald and Bauer, Rupert. "UV-O<sub>3</sub>, UV-H<sub>2</sub>O, UV-TIO<sub>2</sub>, and the Photo-Feton Reaction — Comparison of Advanced Oxidation Processes for Wastewater Treatment." Chemosphere. Volume 28. Number 8. 1994. Pages 1447 to 1454.

Stephenson, Ralph and Blackburn, James. The Industrial Wastewater Systems Handbook. Lewis Publishers. 1998.

- U.S. Environmental Protection Agency. Best Demonstrated Available Technology (BDAT)

  Background Document for Newly Listed or Identified Wastes from the Production of

  Carbamates and Organobromines. March 2, 1995.
- U.S. Environmental Protection Agency. Final Best Demonstrated Available Technology (BDAT) Background Document for Universal Standards: Volume A: Universal Standards for Nonwastewater Forms of Listed Hazardous Wastes. July 1994.
- U.S. Environmental Protection Agency. Final Best Demonstrated Available Technology (BDAT) Background Document for Universal Standards: Volume B: Universal Standards for Wastewater Forms of Listed Hazardous Wastes. July 1994.
- U.S. Environmental Protection Agency. National Risk Management Research Laboratory Treatability Database. Version 5. EPA/600/C-93/003a (1994).
- U.S. Environmental Protection Agency. Final Best Demonstrated Available Technology (BDAT) Background Document for Quality Assurance/Quality Control Procedures and Methodology. October 1991.
- U.S. Environmental Protection Agency. Final Best Demonstrated Available Technology(BDAT) Background Document for U and P Wastes and Multi-Source Leachate (F039): VolumeB: U & P Wastewaters and Nonwastewaters with Methods of Treatment as Treatment Standards.May 1990.

U.S. Environmental Protection Agency. Guidance on Setting Permit Conditions and ReportingTrial Burn Results: Volume II of the Hazardous Waste Incineration Guidance Series - AppendixD. January 1989.

U.S. Filter/Zimpro Products. Product and services information. www.zimpro.com.

Yang, Yiqi, et. al. "Decolorization of Dyes Using UV/H<sub>2</sub>O<sub>2</sub> Photochemical Oxidation." Textile Chemist and Colorist. Volume 30. Number 4. April 1, 1998. p.27.

A 15 A	Tour store and Dente	S D-4- 6	·	N	
Appendix A:	Treatment Per	iormance Data i	or Constituents i	n Nonwastewater Fo	rms oi
Wastes					

Treatment Performance Data for Certain Constituents in Nonwastewaters, Where				
Incineration or Fuel Substitution was Identified as BDAT				
<b>Constituent of Concern</b>	Waste Code(s) Concentration in Tre			
		Waste (mg/kg)		
Aniline	K103, K104	<2.0		
	F039, U012	<5.0 a		
	K083	<5.0 a		
4-Chloroaniline	F039, P024	<5.0 a		
Chloroform <sup>b</sup>	F039, U044, K117, K118,	<2.0		
	K136			
	K009, K010, K019, K029	<2.0 a		
	F025, K021, K073	<2.0 a		

All data are for incineration.

Source: Final Best Demonstrated Available Technology (BDAT) Background Document for Universal Standards Volume A: Universal Standards or Nonwastewater Forms of Listed Hazardous Wastes, EPA, July 1994.

<sup>&</sup>lt; - Indicates a analytical method limit value.

<sup>&</sup>lt;sup>a</sup> - UTS based on these runs.

<sup>&</sup>lt;sup>b</sup> - Chloroform is not a constituent of concern in K181 wastes, but is included here because it was identified in Section 3 as an example of a contaminant that is 'difficult to treat.'

Treatment Performance Data for Certain Constituents in Nonwastewaters, Where				
Thermal Treatment is Employed				
Constituent Name	CAS	Concentration	Percent	Technology Used
	Number	After	Improve-	
		Treatment	ment	
Aniline	62-53-3	<5 ng/L	>99.999	Thermal Destruction

<sup>&</sup>lt; - Indicates an analytical method detection limit value.

Source: EPA NRMRL, 1994 unless otherwise indicated.

Appendix B: Treatment Performance Data for Constituents in Wastewater Forms of Wastes

## Performance of Wet Air Oxidation or Chemical Oxidation

Constituent Name	CAS	Effluent	Percent	Technology
	Number	Concentration	Reduction	Used
Aniline	62-53-3	<0.0093 mg/L	>99.99	Chemical
				Oxidation
4-Chloroaniline	120-71-8	0.12 mg/L	99.8	Wet Air
				Oxidation
o-Dichlorobenzene	95-50-1	0.010 mg/L	98.7	Wet Air
				Oxidation
Napthalene	91-20-3	0.21 mg/L	82.5	Wet Air
				Oxidation
Methanol	67-56-1	1000 mg/L	89.6	Wet Air
				Oxidation
Phenol	108-95-2	>1000 mg./L	99.7	Chemical
				Oxidation

Source: Final Best Demonstrated Available Technology (BDAT) Background Document for
Universal Standards Volume B: Universal Standards or Wastewater Forms of Listed Hazardous
Wastes. EPA, July 1994.

Performance of Carbon Adsorption for Constituents in K181 Wastewaters				
Constituent Name CAS Effluent Percent Technology Used				
	Number	Concentration	Reduction	
Aniline	62-53-3	NR	NR	Carbon Adsorption

Source: Source: Final Best Demonstrated Available Technology (BDAT) Background Document for Universal

Standards Volume B: Universal Standards or Wastewater Forms of Listed Hazardous Wastes, EPA, July 1994.

NR - Not reported